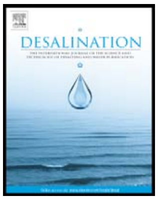
Desalination 250 (2010) 869–875

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal



Phorate degradation by TiO_2 photocatalysis: Parameter and reaction pathway investigations

Ren-Jang Wu [b], Chiing-Chang Chen [c], Chung-Shin Lu [a],*, Peng-Yueh Hsu [b], Ming-Hung Chen [b]

[a] Department of General Education, National Taichung Nursing College, Taichung 403, Taiwan, ROC
[b] Department of Applied Chemistry, Providence University, Taichung 433, Taiwan, ROC
[c] Department of Science Application and Dissemination, National Taichung University, Taichung 403, Taiwan, ROC

ARTICLE INFO

Article history:
Received 9 September 2008
Accepted 27 March 2009
Available online 17 November 2009

Keywords:
Photocatalysis
TiO_2
Phorate
Intermediate
Mechanism

ABSTRACT

The photocatalytic degradation of phorate in aqueous suspensions was examined with the use of titanium dioxide (TiO_2) as a photocatalyst. About 99% of phorate was degraded after UV irradiation for 60 min. The photodegradation of phorate followed pseudo-first-order kinetics and parameters such as pH of the system, TiO_2 dosage, and presence of anions were found to influence the reaction rate. To obtain a better understanding of the mechanistic details of this TiO_2-assisted photodegradation of phorate with UV irradiation, the intermediates of the processes were separated, identified, and characterized by the solid-phase microextraction (SPME) and gas chromatography/mass spectrometry (GC/MS) techniques. The probable photodegradation pathways were proposed and discussed. To the best of our knowledge, this is the first study that reports the degradation pathways of phorate. The electrical energy consumption per order of magnitude for photocatalytic degradation of phorate was also calculated and showed that a moderated efficiency ($E_{EO} = 96$ kWh/(m^3 order)) was obtained in TiO_2/UV process.

1. Introduction

During the last 30 years, organophosphorus pesticides (OPs) have been widely used as an alternative to organochlorine compounds for pest control. OPs represent up to one-third of world pesticide consumption [1]. Organophosphorus compounds exhibit a wide range of toxicity to mammals. They work on the central nervous system, inhibiting its normal function and causing convulsions, paralysis and death [2]. Their presence as contaminants in aquatic environments may cause serious problems to human beings and other organisms. OP residue levels have been detected frequently in environmental waters [3,4], and the need to remove them is urgent.

Phorate [*O*,*O*-diethyl-*S*-[(ethylthio)methyl] phosphorodithioate] is a restricted-use pesticide used to control sucking and chewing pests. Its chemical structure is shown in Fig. 1. It is used in pine forests and on root crops and field crops, including corn, cotton, coffee, and some ornamental plants and bulbs [5]. In 2001, U.S. annual use of phorate was estimated at 3.2 million pounds. The LD_{50} of phorate was reported to be 1.1–2.3 mg L^{-1}, depending on the pathway of intake [6]. Due to its severe acute risk for human health, the WHO has classified phorate as a technical product of extreme hazard. During its use as an insecticide, phorate primarily contaminates the environment through constant leaching and superficial runoff during rainfall.

Titanium dioxide (TiO_2)-based photocatalytic oxidation is a promising technology in water and wastewater treatment because TiO_2 is a cheap, stable, and nontoxic catalyst [7]. It has been shown that solar radiation can be used in photocatalysis, which would make it economically competitive for water and wastewater treatment [8]. The TiO_2-mediated photocatalysis process has been successfully used to degrade pollutants during the past few years [9–11]. The initial step in TiO_2-mediated photocatalysis degradation involves the generation of an (e^-/h^+) pair, leading to the formation of hydroxyl radicals ($^{\bullet}OH$), superoxide radical anions ($O_2^{\bullet -}$), and hydroperoxyl radicals ($^{\bullet}OOH$) as shown below [12,13]:

$$TiO_2 + h\nu \rightarrow TiO_2(h^+ + e^-) \tag{1}$$

$$H_2O_{(ads)} + h^+ \rightarrow {}^{\bullet}OH + H^+ \tag{2}$$

$$OH^- + h^+ \rightarrow {}^{\bullet}OH \tag{3}$$

$$O_2 + e^- \rightarrow O_2^{\bullet -} \tag{4}$$

$$O_{2(ads)} + e^- + H^+ \rightarrow HO_2^{\bullet} \tag{5}$$

The organic pollutants are attacked and oxidized by the radicals formed through the above mechanisms. In addition to hydroxyl radicals, superoxide radical anions—and in some cases the positive holes—are also suggested as possible oxidizing species that could attack organic compounds present at or near the surface of TiO_2 [14].

---

* Corresponding author. Tel.: +886 4 2219 6999; fax: +886 4 2219 4990.
E-mail address: cslu6@ntcnc.edu.tw (C.-S. Lu).

0011-9164/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.desal.2009.03.026

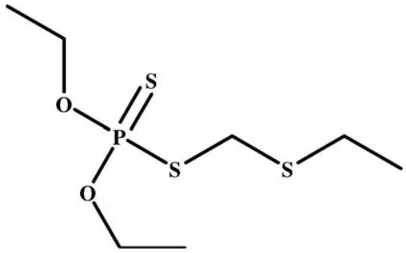


Fig. 1. Chemical structure of phorate.

Little has been reported on the degradation of phorate under UV light in the presence of TiO_2. Doong and Chang [15] investigated the photooxidation of selected organophosphorus pesticides (methamidophos, phorate, malathion, diazinon and EPN) in UV–TiO_2, UV–H_2O_2, and UV–TiO_2–H_2O_2 systems. They used apparent first-order rate constants to describe the degradation behaviors of OPs under different photo systems and indicated that methamidophos and phorate are the easily degradable compounds due to the low energy of P—S and C—S bonds. Chen et al. [16] described a method of preparing TiO_2 supported on fiberglass cloth and discussed the feasibility of photocatalytic degradation of organophosphoros pesticides using supported TiO_2. Their results showed that dichlorvos, monocrotophos, phorate, and parathion could be successfully degraded after 200 min illumination with a 375 W medium pressure mercury lamp.

Although the photocatalytic degradation of phorate has been studied in the past [15,16], very limited information on the photocatalytic intermediates and reaction mechanisms is available. Thus, our study focused on identifying the reaction intermediates and understanding the mechanistic details of the photodegradation of phorate in the TiO_2/UV light process. To the best of our knowledge, this is the first study that reports the degradation pathways of phorate. Moreover, some potential factors likely to influence the photodegradability of phorate have not been well documented. In our study, various parameters that may affect the photodegradation of phorate in the presence of TiO_2 suspensions were also analyzed to obtain a more complete knowledge of TiO_2 photocatalytic efficiency. Since the photodegradation of aqueous organic pollutants is an electric energy-intensive process, and electric energy can represent a major fraction of the operating costs, simple figure-of-merit based on electric energy consumption can be very useful and informative [17]. The electrical energy per order (E_{EO}) was also determined in the TiO_2/UV light process.

Thus, the objectives of the study were (i) to evaluate the kinetics of pesticide disappearance, (ii) to examine the influence of various parameters such as pH of the system, TiO_2 dosage, and presence of anions, (iii) to evaluate the electrical energy efficiency of the studied process, and (iv) to determine the main intermediates by using gas chromatography/mass spectrometry techniques and to propose a degradation pathway.

2. Experimental

2.1. Materials and reagents

Phorate was purchased from ChemService (West Chester, PA) with a purity of 98.0%. Standard solutions containing 12 $mg\,L^{-1}$ of phorate in water were prepared, protected from light, and stored at 4 °C. Diethyl disulfide (Sigma-Aldrich) and ethanol (Merck) were used for intermediate confirmation. Other chemicals were of reagent grade and used as such without further purification. The TiO_2 nanoparticles (P25, ca. 80% anatase, 20% rutile; particle size, ca. 20–30 nm; BET area, ca. 55 $m^2\,g^{-1}$) were supplied by Degussa. Deionized water was used throughout this study. The water was purified with a Milli-Q water ion-exchange system (Millipore Co.) to give a resistivity of $1.8 \times 10^7\ \Omega\,cm$.

2.2. Apparatus and instruments

The apparatus for studying the photocatalytic degradation of phorate has been described elsewhere [18]. The C-75 Chromato-Vue cabinet of UVP provides a wide area of illumination from the 15 W UV–365 nm tubes positioned on two sides of the cabinet interior. Solid-phase microextraction was utilized for the analysis of phorate and intermediates resulting from the photocatalytic degradation process. The SPME holder and fiber-coating divinylbenzene–carboxen–polydimethylsiloxane (DVB–CAR–PDMS 50/30 μm) were supplied from Supelco (Bellefonte, PA). GC/MS analyses were run on a Perkin-Elmer AutoSystem-XL gas chromatograph interfaced to a TurboMass selective mass detector. The ionic by-products from phorate degradation were analyzed using a Dionex ICS-90 ion chromatograph.

2.3. Procedures and analysis

An aqueous TiO_2 dispersion was prepared by adding 50 mg of TiO_2 powder to a 100 mL solution containing phorate at appropriate concentrations. For reactions in different pH media, the initial pH of the suspensions was adjusted by addition of either NaOH or HNO_3 solutions. Prior to irradiation, the dispersions were magnetically stirred in the dark for 30 min to ensure the establishment of the adsorption/desorption equilibrium. Irradiations were carried out using two UV-365 nm lamps (15 W). After each irradiation cycle, the amount of phorate was thus determined by SPME-GC/MS. The aqueous TiO_2 dispersion was sampled (5 mL) and centrifuged to separate the TiO_2 particles. The clear solution was then transferred into a 4-mL sample vial. The SPME fiber was directly *immersed* into the sample solution to extract phorate and its intermediates for 30 min at room temperature, with magnetic stirring at 550 ± 10 rpm on the Corning stirrer/plate (Corning, USA). The fiber was then inserted into the GC inlet to desorb the analytes at 250 °C for 40 min. Separation was carried out in a DB-5 capillary column (5% diphenyl/95% dimethyl-siloxane), 60 m, 0.25-mm i.d., and 1.0-μm thick film. A split-splitless injector was used under the following conditions: injector temperature 250 °C, split flow 10 mL/min. The helium carrier gas flow was 1.5 mL/min. The oven temperature program was 1.0 min at 60 °C, 8 °C/min to 240 °C (16.5 min). Electron impact (EI) mass spectra were monitored from 10 to 350 *m/z*. The ion source and inlet line temperatures were set at 220 and 250 °C, respectively. The standard secondary actinometer (phenol) was determined under identical instrumental conditions, except that the oven temperature program was 6 min at 240 °C.

The ionic by-products from phorate degradation were analyzed using a Dionex ICS-90 ion chromatograph. The column was an IonPac® AS4A-SC (4 mm × 250 mm) for phosphate (PO_4^{3-}) and sulfate (SO_4^{2-}) analyses. The flow rate was 1.0 mL/min, and the injection volume was 100 μL of the filtered reaction samples. The eluent consisted of a mixture of 3.5 mM Na_2CO_3 and 1 mM $NaHCO_3$ for the anion analysis. For these operating conditions, the retention times for PO_4^{3-} and SO_4^{2-} were 5.4 and 6.7 min, respectively. For quantitative studies, standard solutions and calibration curves for each ion were prepared in the range from 1 to 10 mg L^{-1}. In order to avoid adsorption of the anions on the surface of the catalyst during the reaction, a desorption procedure was applied. This consisted of the addition of NaOH (1 N) to the reaction mixture after irradiation until it had reached a pH of 12.

3. Results and discussion

3.1. Photodegradation kinetics

Many authors [15,19,20] have reported that the TiO_2 photocatalytic degradation of organophosphorus compounds follows first-order kinetics. The photocatalytic degradation of phorate is presented in Fig. 2 while, in the inset, the logarithm of the ratio of the initial concentration (C_0) to the concentration at a given time (C) versus time